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METHODS FOR THE STUDY OF ABSORPTION SPECTRA OF COLLOIDAL SOLUTIONS OF CONSIDERABLE THICKNESS

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The dispersal of radiation in a light-diffusing medium is described by a transfer equation which links the parameters of the radiation field with the properties of the medium itself [1-3]. Having measure the parameters of the radiation field, it is possible to find the basic characteristics of the medium, for example, the absorption coefficient α and, correspondingly, the dispersion factor σ. However, it is not always possible to select radiation parameters which are convenient for experimental determination and would provide a simplified solution of the transfer equation, and an unambiguous determination of values α and σ. These difficulties were successfully eliminated in papers [4-6]:

$$\alpha = K'\bar{\mu}, \tag{1}$$

where K' is the depth damping factor,

$$\bar{\mu} = \frac{E_1 - E_2}{E_0} \tag{2}$$

is the mean cosine of the inclination of the radiation beam. Value $\bar{\mu}$ can be determined experimentally, since

$$E_1 - E_2 = 2\pi \int_{-\pi/2}^{+\pi/2} B(\theta) \sin\theta \cos\theta d\theta$$

is the difference of radiation of the horizontal field from the top and from the bottom, and

$$E_0 = 2\pi \int_{-\pi/2}^{+\pi/2} B(\theta) \sin\theta \, d\theta$$

is the spatial radiation--i.e., the radiant flux, passing through the sphere of unit radius [9]. The depth damping factor K' is found on the basis of the fact that in a thick sample the luminance of the B flux decreases with an increase of depth t according to the exponential law

$$B(t, \theta) = B(t_0, \theta) e^{-K'(t-t_0)}. \tag{3}$$

Thus, by measuring K', E_1, E_2, and E_0 in a thick dispersing medium, it is possible, using equation (1) to immediately find α--i.e., the true volumetric absorption factor of this medium. The correctness of equations (1), (3) is substantiated by experimental results [10-15]. Here the value $\bar{\mu}$ is calculated by the methods of graphic integration of the indicatrix of luminance in a thick sample which are measured by various hydrophotometers. This method of finding $\bar{\mu}$ is quite cumbersome, requiring many measurements. In addition, because of their cumbersomeness, the hydrophotometers which are used [10-15] distort, to some degree, the true dispersion of luminance of the radiation field which can lead to erroneous

values $\bar{\mu}$.

For a simple and more precise determination of values K', $\bar{\mu}$, and, this means also the value α, we have designed a unit, the diagram of which is shown in Fig. 1a. Its basic part is a cylindrical tank (1) whose height and diameter are 50 cm, and whose inner walls have a reflection coefficient of 0.6-0.7 order. In the center of the tank, waterproof plugs (2) are used to attach the detectors: the spherical detector (Fig. 1b), for measuring the spatial radiation and the flat detector for measuring the radiation in the horizontal field. The recording of light signals from the detectors is executed with the application of the FEU-38 photomultiplier (3) and a UF-206 counter (4). The photomultiplier is fed from the VSF high voltage regulator (7). A valve is installed on the bottom of the tank and used during measurements to gradually lower the level of the investigated liquid shown on the scale (9) of the water meter (10). Monochromatization of radiation is executed by means of exchangeable interference filters (11).

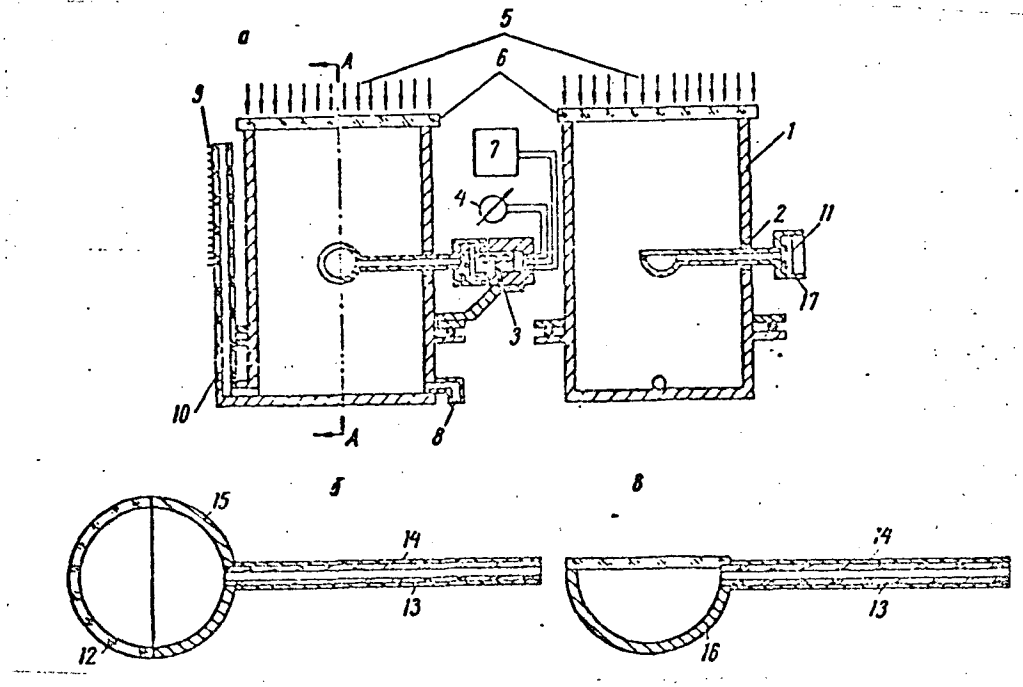

Fig. 1. Diagram of the unit (a) and the design of the detectors: Spherical (b) and flat (c)

The colloidal solution under investigation is irradiated from the top by a direct uniform light flux (5). To prevent dirt from entering the tank, it is covered by a regular window glass (6). The spherical detector (Fig. 1b) is a milky frosted glass ball (12) with a one centimeter radius to which a light conductor is attached. A brass pipe (14) is placed on the light conductor and attached to the opaque cap (15) which is coated with white nitro-enamel.

This design of the detector makes it possible to measure only the half-spatial radiation. The spatial radiation is found by doubling the obtained results since in a deep sample there exists an azimuthal symmetry of the light field [7, 8].

The flat detector (Fig. 1c) is a milky hemisphere of about one centimeter radius, closed from the outside by an opaque cap (16), which is also coated with nitro-enamel. The hemisphere is attached to the milky glass which is frosted from both sides. The light conductor is the same as in the spherical detector. To link the light conductors with the photomultiplier case, lightproof plugs (17) are used. The length of the light conductors is selected so that the centers of the detectors when operating are in the center of the tank. Light detectors can easily move to the side wall of the tank and rotate around the optical axis of the light conductors. The photomultiplier is attached to the tank is such a way that it can be linked alternately to the light conductors of both detectors.

The detectors were checked as follows: the spherical detector for isotropy --i.e., for independence of their factors from the region of the fall of the radiation flux on the surface of the sphere; the flat detector for the correspondence of measurements of its factors according to the cosine law to the change in the fall of the direct radiation flux. The measurements were conducted on a goniometer by means of a thin beam. Maximum deviations from isotropy for the spherical detector were about 8 to 10 per cent. In checking the horizontal detector it was found that on the edges of its sensitive area the deviation of indications from the cosine law increases. Therefore, the area was decreased in half by means of diaphragming so that the central portion, where the deviations did not exceed 5 to 7 per cent would remain open. Thus it can be considered that the sensitivity of the horizontal detector is almost independent of the contitions of its radiation. The sensitive surface of the spherical detector was also decreased in half.

The detectors which were and checked in this manner are used for measuring values E_1, E_2, and E_0. The readings obtained from the flat detector are proportional to the exposure of the horizontal field, and the readings from the spherical detector, to the half-spatial radiation --i.e.,

$$N_1 = C_1E_1;\ N_2 = C_1E_2;\ N_3 = C_2E_0, \tag{4}$$

where C_1 and C_2 correspondingly are the proportionality factors for the flat and sphereical detectors, the coefficient C_2 includes also the 0.5 multiplier.

From (2) and (4) it follows that

$$\alpha = K' \frac{N_1 - N_2}{\eta N_3}, \tag{5}$$

where $\eta = C_1/C_2$.

It is known [9] that the spatial radiation is a sum of normal radiations in the given point of space, taken in all possible directions for the total solid angle

4 π. Therefore, if the normal radiation is created only by one point source, numerically it is equal to the spatial radiation created by the same source in the same point in space. From here stems the method of finding the factor η in the equation (5): if the flat and spherical detectors are irradiated with a source located at a sufficiently long distance from them (40 to 50 times greater than the linear dimensions of the source and the detectors), between their indications N'_1, N'_2 and the corresponding coefficients C_1 and C_2 the following equation will result

$$\frac{N'_1}{N'_2} = \frac{C_1}{C_2} = \eta. \qquad (6)$$

Table 1

Spectral Dependence of the Coefficient η for the Detectors Used in the Unit

λ nm*	400	450	500	550	600	650
η	2.9	1.8	1.58	1.7	1.65	1.5

*nanometer

This is true if the value of the sensitive area of the flat detector is equal to the area of the main section of the spherical detector and if the measurements are conducted in the same point. We found values of the factor η for every 50 nanometers in the region of 400 to 800 nanometers. They are shown in Table 1.

For determining α the following method is used. The tank is filled with the colloidal solution being investigated to the level which is 15 to 20 cm above the level where the detectors are attached. Valve 8 is opened and, by means of the flat detector, readings are taken which correspond to the relative radiation intensity when the height of the column of liquid t is lowered above the detector in specific intervals (for example every one centimeter) until t=0. The dependence $\ln \frac{B(t)}{B(0)} = f(t)$ is constructed which according to

equation (3) must represent a curve with an angular factor K' within the limits of values t, where the thick sample is used. Fig. 2 shows these dependencies for a colloidal medium based on vitreous powder. The powder which was suspended in glycerin according to the Stokes method, with a mean statistical particle size of about 15 microns, was added to the solution, the viscosity and density of which was selected so that it would be possible to disregard the settling of the powder particles during measurements. Before each series

of measurements the colloidal medium was thoroughly mixed. Fig. 2 shows that with an increase of powder concentration the inclination toward the abscissa axis of the straight portions of the curves increases--i.e., the depth damping factor K' grows.

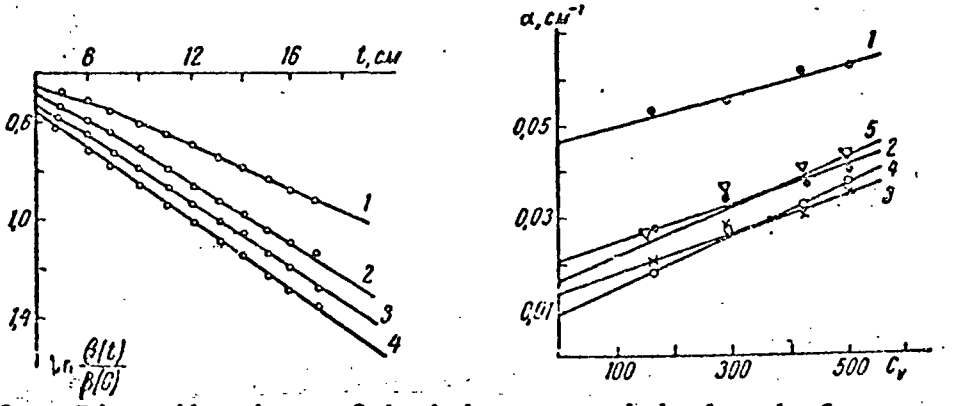

Fig. 2. Distribution of brightness with depth for a dispersing medium with different concentrations of the vitreous powder per 10 liters of liquid: 1 - 4g; 2 - 7; 3 - 10; 4 - 12; λ =500 nanometers

Fig. 3. Dependence of the volumetric absorption factor α of the dispersing medium on the volumetric concentration $C_v \cdot 10^{-6}$ of the vitreous powder in the medium: 1 - λ =400 nanometers; 2 - 500; 3 - 550; 4 - 600; 5 - 650

Table 2

Spectral Dependence of the Absorption Factor α^* for Measurements of an Undispersed Uniform Liquid

λ, nm	400	450	500	550	600	650
α_1^*	0.0546	0.0308	0.021	0.012	0.0092	0.014
α_2^*	0.0465	0.0315	0.02	0.013	0.009	0.016

To minimize the effect of the side walls of the tank, the measurements were conducted in such media where the sample became thick at heights t_0, smaller than the tank's radius, and in which the thickness of a 25 cm layer would be "infinite" within a 5 to 10 per cent accuracy. On the other hand, the concentration of the powder must not be too high, since in such case the results of measurements will be affected by the finiteness of the dimensions of the radiation detector.

Following this, in the region of values t_0, where a thick sample is realized, the readings N_1, N_2, and N_3 were taken alternately for each of the colloidal solutions being investigated. Later, according to equation (5), the values of the volumetric absorption factor α were calculated. Fig. 3 shows the dependency curves α on the concentration of powder in liquid C_v. A direct proportional dependence is evident. This was to be expected since [16]

$$\alpha = \pi r^3 b \alpha_{sub} N, \qquad (7)$$

where N is the number of powder particles in a unit volume; b is the form factor of the vitreous particles; r is their radius. The latter does not depend on N (or C_v). Evidently the sections intercepted by curves $\alpha = f(C_v)$ from the axis of the ordinate must yield the value of the volumetric absorption factor selected for preparing the dispersing liquid medium, α_2^*. Actually in comparing values α_1^*, obtained by direct measurements (using the SF-4) of transparent liquid without powder, with their values taken from the corresponding curves in Fig. 3, it follows that they correspond sufficiently well (Table 2). In addition from equation (7), it is evident that since b does not depend on λ, the spectral range of the absorption factor of the vitreous particle substance α_{sub} must be established by the spectral range of the values of the tangents of the slopes of the curves $tg\phi$ shown in Fig. 3. For this reason, Fig. 4 shows the spectral dependence of the absorption factor α_{sub} obtained by measuring (using the SF-4) the solid uniform glass plate used for preparing the powder, and also the dependence $tg\phi = f(\lambda)$, reduced to value α_{sub} for λ = 550 nanometers. A sufficiently good agreement of the spectral range of the given curves and the above-mentioned agreement of the values α^* (see Table 2) attest that the unit and the method of measurements described here can be successfully used for investigating the absorption spectra of various light dispersing media which, of course, satisfy the specifications mentioned above.

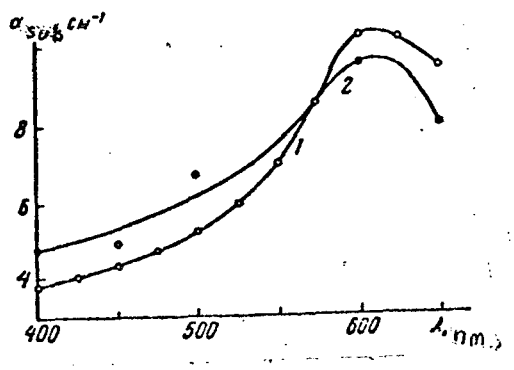

Fig. 4. Spectral dependence of the absorption factor α_{sub} of glass obtained using the SF-4 (1) and the described unit (2)

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